III.B.9 Effects of Recycle on Catalytic Fuel Reforming

Objectives

- Study the effects of recycle streams on reforming properties.
- Evaluate anode versus reformer recycle configuration.
- Delineate the effects of individual components present in recycle streams.

Accomplishments

- Evaluated the effects of anode recycle ratios of 0 to 0.5 on reforming properties (yields of H_2, CO, CO_2, and unsaturates, hydrocarbon conversion, and carbon formation). A similar study was also completed for the reformer recycle stream.
- Studied the effects of individual components present in the recycle streams (H_2, CO, CO_2, H_2O, and N_2) on reforming properties.

Introduction

The U.S. Department of Energy is sponsoring development of high-temperature fuel cell power systems based on solid oxide technology through its Solid State Energy Conversion Alliance (SECA) Program. The program is geared at mass manufacturing of fuel cells for high volume markets and multiple applications. One of those markets/applications is a diesel-fueled auxiliary power unit (APU) for long-haul truck transportation. The fuel processor is a critical component of this system and must be able to provide a clean, tailored synthesis gas to the fuel cell stack for long-term operation. Key characteristics desired for the processor (and the system) include low cost, high efficiency, maximum thermal integration, low maintenance intervals, and acceptable startup and transient response. There are also several barrier issues that must be overcome to achieve these characteristics. Carbon formation must be minimized to avoid coking of the catalysts in the reformer and downstream fuel cell. Water can help

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suppress carbon formation, allow for better thermal integration and system efficiency, and possibly inhibit temperature rise and catalyst sintering. However, the National Energy Technology Laboratory (NETL) is promoting "dry" systems to reduce cost and complexity of overall fuel cell systems. On-board water storage is not an attractive option for many applications including APUs. Therefore, in this study, we explored two possible configurations (see Figure 1) to incorporate higher water concentrations in a "waterless" system: (1) recycle from the reformer exit and (2) recycle from the anode exit back to the reformer inlet. A comparison of these two configurations in terms of reforming properties (yields of H_2, CO, CO_2, paraffins, and unsaturates [C1-C6 olefins and benzene], hydrocarbon conversion, and carbon formation) is presented. The effects of individual recycle components (H_2, CO, CO_2, N_2, and H_2O) on reforming properties are also reported.

Approach

NETL's SECA Fuel Cell Program requires that the fuel reformer must operate without any onboard water storage to reduce costs as well as overall complexity of the fuel cell system. However, the presence of water in the feed to the reformer is critical in reducing carbon formation on the catalyst surface. Steam facilitates cleaning of the carbon as it forms (Reaction 1) and thus helps in reducing carbon formation on the catalyst.

$$C + H_2O = CO + H_2 \qquad (1)$$

Water is a main product along with CO_2 on the fuel cell anode. Therefore, recycling a portion of the anode exhaust stream to the reformer can be a potential onboard source of water. Additionally, CO_2 present in the exhaust stream can be beneficial too. The presence
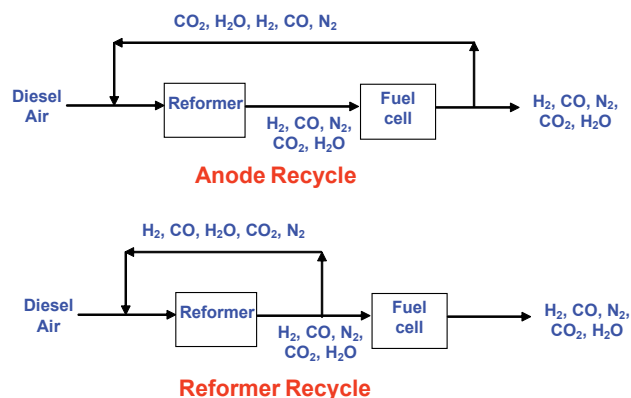

FIGURE 1. Recycle Configurations

of CO_2 in the system can help in reducing carbon formation by the Boudouard reaction:

$$C + CO_2 = 2CO \qquad (2)$$

In addition to coke inhibition, CO_2 and H_2O can serve as oxidants for reforming reactions and, thus, increasing hydrocarbon conversion through dry and steam reforming, respectively, of unconverted hydrocarbons in the reformer. Consequently, a lower O/C ratio can also be used. Overall, water can help suppress carbon formation, allow for better thermal integration and system efficiency, and possibly inhibit temperature rise and catalyst sintering.

The reformer recycle stream was also studied as a potential source of water. In this configuration, a part of the reformer exhaust – consisting mainly of CO, H_2, N_2, some water, CO_2, and unconverted lower hydrocarbons – is recycled back to the reformer. It is speculated that H_2 in this stream may check the hydrocarbon dehydrogenation on the catalyst surface, which is believed to be a coke forming reaction.

A mixture of 40 wt% tetradecane, 20 wt% t-butylbenzene, 18 wt% t-butylcyclohexane, and 22 wt% decalin was used as a surrogate diesel fuel for this study. A simulated stream of 24% CO_2, 18% H_2O, 3% H_2, 3% CO, and 52% N_2 was used as anode recycle stream whereas a composition of 24% CO, 22% H_2, 5% H_2O, 1% CO_2, and 48% N_2 was used as a reformer recycle stream. These compositions were estimated using equilibrium calculation based on the surrogate diesel fuel. Also, 80% conversion of syngas in the fuel cell was assumed for the anode recycle stream. However, higher water composition than calculated was used for the reformer recycle stream since it was not possible to pump the water accurately with lower flow rates. Simulated recycle stream and air feed gases were delivered by mass flow controllers and the liquid feeds were delivered by a high accuracy high performance liquid chromatograph (HPLC) dual pump. A recycle ratio range of 0-0.5 was studied for both configurations. These runs were carried out in a fixed bed continuous-flow reactor. Experiments were conducted at an O/C of 1.0, a gas hourly space velocity (GHSV) of 50,000 h^{-1}, and 850°C. γ-Alumina supported rhodium (0.5 wt%) catalyst (surface area 100 m^2/g) was used in this study as a base catalyst. The catalyst was diluted with 5/1 quartz sand-to-catalyst ratio (by weight) to avoid preferential gas flow paths and hot spots. Temperature programmed oxidation (TPO) of the spent catalyst was used to determine the amount of carbon formed during reforming reactions.

The gases (N_2, O_2, CO, CO_2, and CH_4) were analyzed using a Thermo Onix mass spectrometer. The gaseous hydrocarbon products (C_1-C_6 paraffins, C_2-C_6 olefins, and benzene) were analyzed using a HP5890 gas chromatograph equipped with a flame ionization detector. Yield of product A (H_2, CO, and CO_2) is defined as:

$$\text{Yield of A (\%)} = \frac{\text{Moles of A produced x 100}}{\text{N x moles of hydrocarbon fed to the reactor}}$$

Where, N is the number of moles of hydrogen/mole of hydrocarbon for H_2 yields and is the number of carbons in hydrocarbon fuel for yields of other products. The conversion of hydrocarbons is defined as:

$$\text{Conv (\%)} = \frac{(CO + CO_2 + \sum_{i}^{i=1-7} iC_iH_r) \times 100}{\text{N x moles of hydrocarbon fed to the reactor}}$$

Results

Effects of Anode Recycle Stream

Yields of H_2, CO, CO_2, lower paraffins and saturates for anode recycle ratios 0 to 0.5 are shown in Figure 2. H_2 and CO yields increased with increasing anode recycle ratio. However, yields of CO_2, paraffins, and unsaturates (C2-C6 olefins + benzene) generally decreased with increasing anode recycle ratio. Negative CO_2 yields (or CO_2 conversion) and >100% CO yields at an anode recycle ratio of 0.2 and above suggest that high concentrations of CO_2 present in the system at higher recycle ratios facilitate the reverse water gas shift reaction ($CO_2 + H_2 = CO + H_2O$). However, H_2 yields increased instead of decreasing as expected from the reverse water gas shift reaction because lower hydrocarbons which were significantly observed at lower recycle ratios were converted in the presence of additional oxidants such as water (steam reforming) and CO_2 (dry reforming) in the feed, thus contributing to increasing H_2 yields as well as to lowering yields of lower hydrocarbons. Liquid hydrocarbon conversion to gaseous products was always close to 100%.

One significant performance difference observed for different recycle ratios was the carbon formation on the catalyst. The amount of carbon deposited on the catalyst
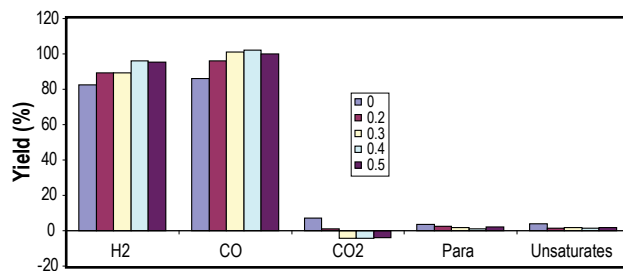
FIGURE 2. Effects of Anode Recycle on Product Distribution

is given in Figure 3 for different recycle ratios used in this study. Interestingly, the carbon formation can be related to unsaturates yield, which generally decreased with increasing anode recycle ratio. The TPOs of carbon deposited on the catalyst at different recycle ratios are shown in Figure 4. Mainly, two peaks were observed in the TPOs of the catalyst used for different recycle ratios. The low temperature peaks (~600°C) can be assigned to carbon deposition on rhodium metal sites, which can be oxidized easily at low temperatures [1]. The high temperature peaks (~800°C) can be attributed to carbon deposited on the support. There was not a certain trend observed for the low temperature peaks with recycle ratio. However, the highest area under the low temperature peak was observed when no recycle stream was used, and the lowest area under the low temperature peak was observed when the recycle ratio was 0.5. On the other hand, the size of the high temperature peaks significantly decreased with increasing anode recycle ratio and only a small hump was observed for anode recycle ratios of 0.4 and 0.5. This suggests that the amount of carbon deposited on the support which is more refractory in nature can be reduced in the presence of a recycle stream.
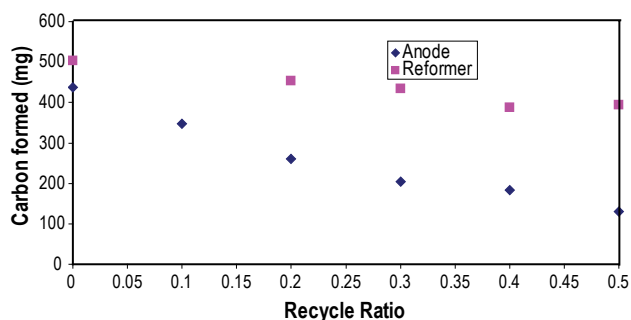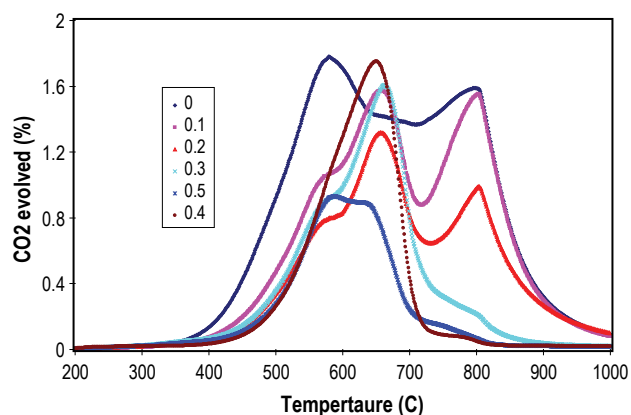
Effects of Reformer Recycle Stream

Yields of H_2, CO, CO_2, lower paraffins, unsaturates, and liquid hydrocarbon conversion for reformer recycle ratios 0 to 0.5 are shown in Figure 5. Effects of reformer recycle which was mainly comprised of CO and H_2 were significantly different than the anode recycle. Contrary to anode recycle, H_2 and CO yields and liquid hydrocarbon conversion considerably decreased upon introduction of a reformer recycle while the yields of lower paraffins, unsaturates, and CO_2 increased in the presence of the reformer recycle. Carbon formation was not affected much by introducing a reformer recycle stream (Figure 3).

Effects of Individual Components

Components present in both recycle schemes were the same, but with completely different compositions. Therefore, some of those components may have detrimental effects on the reforming properties while others may have positive effects. To delineate the effects of each recycle component, experiments were conducted to examine the effect of individual components (N_2, H_2, CO, H_2O, CO_2) present in the either of recycle streams on the performance of fuel reforming catalyst. These runs with individual components were conducted using a flow rate equivalent to the recycle ratio of 0.4 and the composition of the simulated recycle stream was 21 vol% of individual components balanced by N_2. In the case of N_2, the whole stream was comprised of only N_2 and this inert stream was used as a baseline for comparison proposes.

The effect of individual components on carbon formation is shown in Figure 6. The presence of CO_2 and H_2O in the recycle stream significantly decreases carbon formation compared to N_2 only in the recycle stream. As mentioned earlier, the presence of CO_2 in the system helps in reducing the catalyst carbon formation by Boudouard reaction ($C + CO_2 = 2CO$), whereas the carbon can be steam-cleaned as it forms in the presence of water in the system ($C + H_2O = H_2 + CO$) and, hence, reducing the amount of carbon formed. The presence

FIGURE 3. Effects of Recycle on Carbon Formation

FIGURE 4. Effects of Recycle on Carbon Formation Type: Anode Recycle
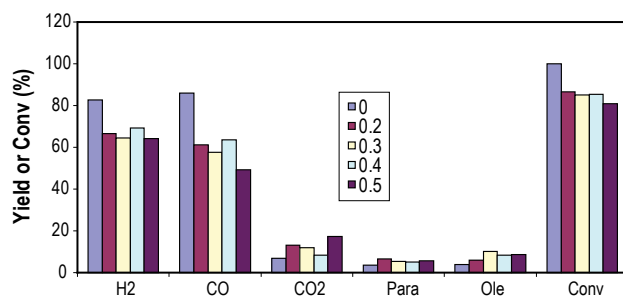

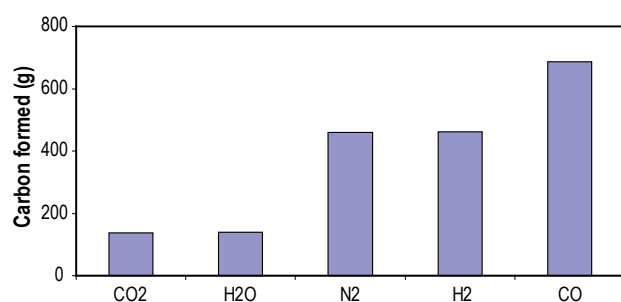**FIGURE 5.** Effects of Reformer Recycle on Product Distribution

FIGURE 6. Effects of Individual Recycle Components on Carbon Formation

of CO only in the recycle stream considerably increased the amount of carbon formed compared to N_2 only in the recycle stream. Higher CO concentrations facilitate the Boudouard carbon formation and, thus, produce more carbon. Also, the presence of CO may poison the active metal sites and, hence, produce higher amounts of unsaturates due to enhanced gas phase chemistry which results in higher amounts of carbon on the catalyst surface. However, H_2 in the recycle stream has no effects on carbon formation.

Conclusions

- This study was conducted to evaluate the effect of the addition of a recycle stream (from anode and reformer) on the performance (conversion, selectivity, deactivation, etc.) of the fuel reforming catalyst.

- H_2 and CO yields increase while carbon formation decreases with increasing anode recycle ratio.

- H_2 and CO yields, as well as hydrocarbon conversion, decrease with increasing reformer recycle ratio while carbon formation does not change significantly.

- Effect of individual components (CO, CO_2, H_2, and H_2O) present in the recycle stream on the reforming properties compared to N_2 only in the recycle stream: H_2 – no effect, CO – negative effect, CO_2 and water – similar positive effect on carbon formation. CO in the recycle stream enhances carbon formation.

FY 2006 Publications/Presentations

1. D. Shekhawat, T. H. Gardner, D. A. Berry, J. J. Spivey, Catalytic Reforming of Liquid Hydrocarbon Fuels for Fuel Cell Applications, *Catalysis,* Royal Society of Chemistry, Cambridge, UK, Vol. 19, Chapter 6, 184-253.

2. D. Shekhawat, D. A. Berry, T. H. Gardner, Diesel Fuel Reforming Studies, 2006 NETL Fuel Reforming Annual Merit Review, May 4, 2006.

References

1. Shamsi, A., Baltrus, J. P., and Spievy, J. J., 2005, Appl. Catal. A: Gen., 293, pp. 145-152.